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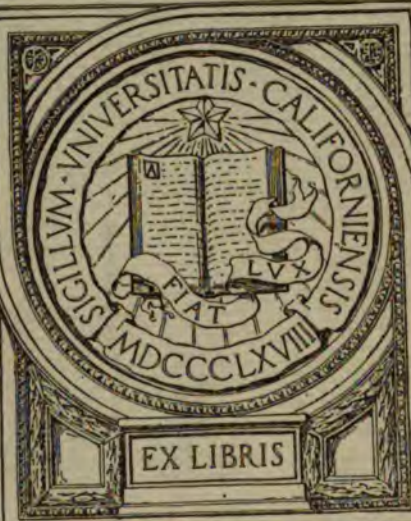
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**A Comparative Study of the Reactions of
Nitrosophenol and N-Chloroquinonimine
with Aromatic Amines**

DISSERTATION

**PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIRE-
MENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN THE GRADUATE SCHOOL OF THE OHIO
STATE UNIVERSITY**

BY

CARLETON EDGAR CURRAN

Dupont Fellow, 1918-19, 1919-20

**THE OHIO STATE UNIVERSITY
1921**

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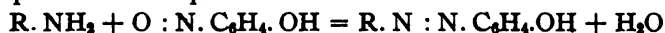
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INTRODUCTION

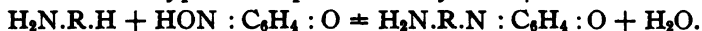
Nitrosophenol may be caused to react with primary aromatic amine without difficulty. The variety and character of the condensation products, however, do not serve to indicate clearly the manner in which the reaction proceeds. Indeed, consideration of the facts from varying stand-points might lead to opposite interpretations.

The tautomerism displayed by nitrosophenol, which under varying conditions may function either as a true phenol or as quinone oxime, suggests at least three very interesting possible reactions:

(1) Nitrosophenol, acting as a true phenol, may condense with the amine to produce an azophenol:



(2) With nitrosophenol functioning as an oxime condensation might conceivably result in the combination of a hydrogen atom from the amine nucleus with the hydroxyl of the oxime group, forming an indophenol. Compounds of this type are important as dyestuffs.



(3) Or again, condensation might be effected in such a manner as to produce a quinone hydrazone:



Experimental evidence may be adduced to support each of these possible reactions.

It has long been known that certain tertiary aromatic amines will react in accordance with reaction (2), indophenols or indamines being formed. A similar reaction is said to be employed by commercial dye manufacturers wherein primary amines and nitroso compounds are used as raw materials. However, reviewing the literature of previous investigations discloses very little information relative to such reactions. The object of this work has been, therefore, to study the condensation taking place between nitrosophenol and the aromatic amines, especially aniline and *p*-toluidine, in order to discover the mechanism of the reaction.

Three lines of experimental work were found necessary in the course of the investigation, as follows:

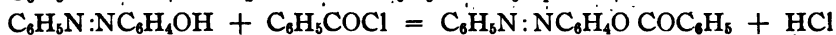
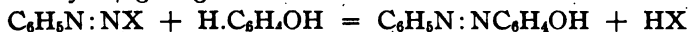
1. A study of the mineral acid salts of phenylazophenol (hydroxyazobenzene), and their reaction with aniline.
2. A study of the course of the reaction between nitrosophenol and the aromatic amines, with the isolation and identification of the various reaction products.
3. A comparative study of the reaction between *N*-chloroquinonimine (quinonechlorimide) and the aromatic amines, because of the similarity of constitution of the former to that of nitrosophenol.

In the following a brief outline of the historical development of each of these fields is given. A statement of the results of the experimental work follows, together with conclusions to be drawn therefrom. A report of the actual experimental methods and data completes the paper.

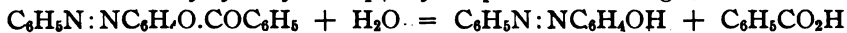
I

THE CONSTITUTION OF THE SALTS OF PHENYLAZOPHENOL

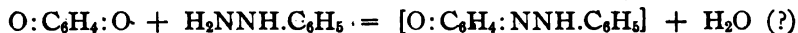
The commonly accepted configuration for phenylazophenol follows from its synthesis by the reaction of diazonium salts with phenol in alkaline solution¹ and the ready formation of its esters with the various acylating and alkylating reagents.²



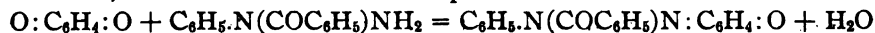
This ester is readily hydrolyzed to phenylazophenol according to the reaction:



However, investigations of the acylated hydrazones of quinone have had a considerable part in determining the true nature of phenylazophenol. Zincke³ pointed out that free phenylhydrazine, or its salts, reacts with quinone with decomposition and evolution of gases, although the following reaction might be expected:



When certain substituted hydrazines, *i. e.*, the unsymmetrical acyl derivatives, are used normal reaction products are obtained:

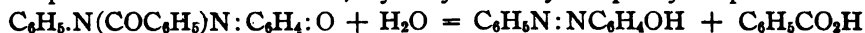


¹Griess, *Ann.* 137, 84 (1866); Kekule and Hidegh, *Ber.* 3, 234 (1870); Dimroth, *ibid.* 35, 2862.

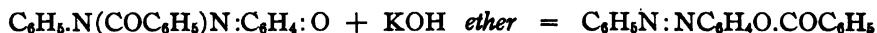
²Tschirwinsky, *Ber.* 6, 561 (1873); McPherson, *Am. Chem. J.* 22, 364 (1899).

³Zincke, *Ber.* 16, 1563 (1883).

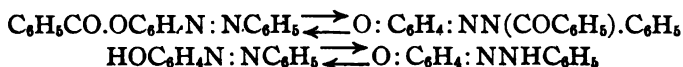
These compounds, which are isomeric with the true esters of phenylazophenol mentioned above, hydrolyze easily to phenylazophenol:



The relationship existing between these unsymmetrical acylphenylhydrazones and the true esters of phenylazophenol was largely cleared up by the work of McPherson and others¹ by synthesis and comparison of the two isomeric forms. Willstätter and Veraguth² accomplished the direct conversion of one form to the other by the action of powdered potassium hydroxide upon quinone α -benzoylphenylhydrazone in absolute ether:

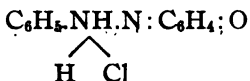


The results of these investigations proved that the acyl ester of phenylazophenol and quinone α -acylphenylhydrazone are tautomers. Similar reasoning may be applicable in explaining the true nature of phenylazophenol. That is, phenylazophenol is tautomeric with quinone phenylhydrazone. The relationship may be best shown by the following formulas:



This tautomeric explanation is especially interesting in the light of investigations of the action of concentrated mineral acids upon phenylazophenol.

Hantzsch³ has prepared and isolated the hydrochloride of phenylazophenol and has assigned to it the configuration of a quinone phenylhydrazone:



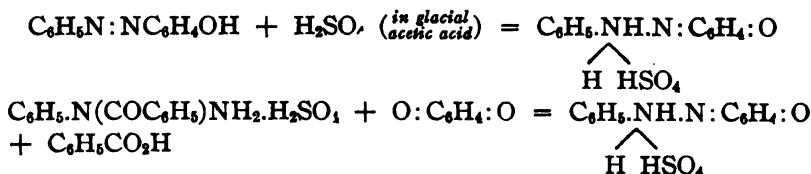
It has been noticed by McPherson and Dubois⁴ that a similar salt is formed either by the action of sulfuric acid upon phenylazophenol or of α -benzoylhydrazine sulfate with quinone:

¹McPherson, *Am. Chem. J.* 22, 364 (1899); McPherson and Gore, *ibid.* 25, 485 (1901); McPherson and Dubois, *J. Am. Chem. Soc.* 30, 816 (1908); McPherson and Fischer, *ibid.* 22, 141 (1900).

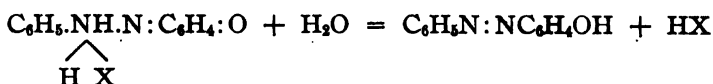
²Willstätter and Veraguth, *Ber.* 40, 1432 (1907).

³Hantzsch, *ibid.* 32, 3091 (1899).

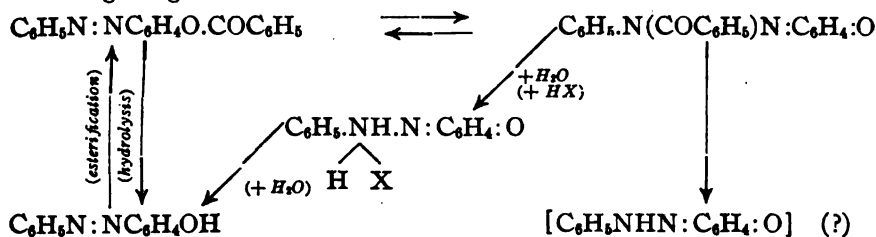
⁴McPherson and Dubois, *J. Am. Chem. Soc.* 30, 816 (1908).



Both the hydrochloride and the sulfate are readily hydrolyzed to phenylazophenol.



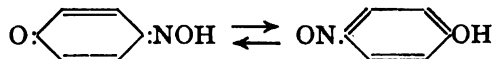
The foregoing reactions undoubtedly established the constitution of the mineral acid salts of phenylazophenol; and also the tautomerism of phenylazophenol and quinone phenylhydrazone. The relationships existing between the various derivatives are briefly summarized in the following diagram:



II

THE REACTION OF NITROSOPHENOL WITH AROMATIC AMINES

Nitrosophenol, or quinone oxime, was first prepared by Baeyer and Caro¹ by the action of *p*-nitrosodimethylaniline with alkalis. The isomerism between this compound and the product of hydroxylamine salts upon quinone was later established by Goldschmidt, Wurster² and others, and it is now generally conceded that the phenolic and ketonic, or oxime, modifications exist in tautomeric relation:



¹ Baeyer and Caro, *Ber.* 7, 809 (1874).

² Goldschmidt, *ibid.* 17, 213 (1884); *ibid.* 801; Wurster, *ibid.* 20, 2632 (1887).

In alkaline solution the phenol tautomer predominates and a number of salts, or phenolates, are known. In acid mediums the compound functions as an oxime.

The reaction between nitrosophenol and aromatic amines was first studied by Kimich¹ in 1875. By heating aniline acetate with nitrosophenol at 90–100° for half an hour he obtained a solid reaction product. When this was extracted with dilute ammonia and the ammoniacal solution acidified with dilute acetic acid a yellow compound was precipitated which Kimich identified as phenylazophenol. The solid remaining could not be purified completely and the best sample obtainable analyzed to the formula $C_{10}H_{10}N_2O$, which was named "azophenine" on the supposition that it was an azo derivative. From *p*-toluidine he obtained some *p*-tolylazophenol and the toluidine homolog of azophenine.

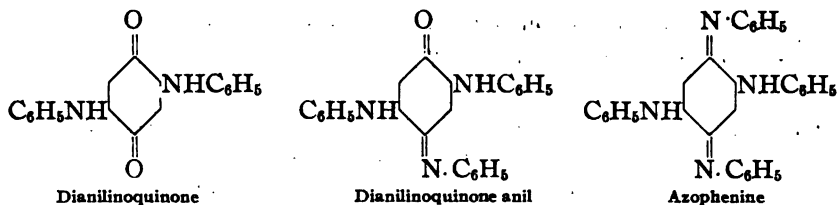
Witt² and others, incidental to experiments on the preparation of the induline dyestuffs, obtained a compound by the action of aniline upon *p*-aminoazobenzene which corresponded very closely to the substance described by Kimich. They repeated Kimich's work but altered his procedure by heating the nitrosophenol with both aniline and aniline hydrochloride for twenty-four hours. This resulted in a largely increased yield of azophenine which proved identical with their compound. Their analysis showed that it contained no oxygen. They concluded, therefore, that the method used by Kimich in purifying his product had been inefficient and that azophenine was an azo derivative with an empirical formula $C_{10}H_{10}N_2$.

O. Fischer and Hepp,³ also working upon the indulines, have prepared azophenine by the action of aniline and aniline hydrochloride with *p*-nitrosodiphenylamine, and also by similar action upon a number of nitroso derivatives. They were impressed by the similarity of these reactions with those incident to the preparation of the anilinoquinones and eventually discovered that the so-called azophenine was in reality dianilinoquinone dianil. The close relationship existing between dianilinoquinone, dianilinoquinone anil, and azophenine, or dianilinoquinone dianil, was observed and pointed out.

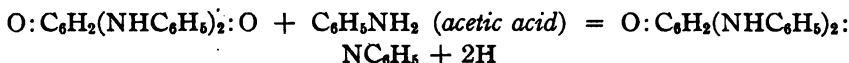
¹ Kimich, *Ber.* 8, 1026(1875).

² Witt, *ibid.* 10, 1311 (1877); *ibid.* 20, 1528 (1887); Witt and Thomas, *J. Chem. Soc.* 43, 115 (1883).

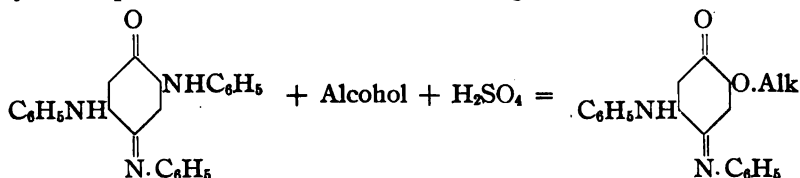
³ Fischer and Hepp, *Ber.* 20, 2479 (1887); *ibid.* 21, 676(1888); *ibid.* 2617; *Ann.* 256, 233–63 (1890); *ibid.* 262, 237 (1891).



The conclusions of Fischer and Hepp were based upon experiments which have sufficient bearing upon our problem to justify a restatement of them at this point. Zincke and von Hagen¹ had clearly shown the relation between dianilinoquinone and dianilinoquinone anil by condensing the former with aniline acetate, forming the anil:



They had also demonstrated the general application of this reaction by carrying it on with various other quinones and amines. Zincke and von Hagen further noticed that when dianilinoquinone anil was treated with concentrated sulfuric acid and ethyl or methyl alcohol an alkyl-oxyanilinoquinone anil was formed according to the reaction:



Fischer and Hepp found that the latter products were also obtained when they acted upon azophenine with sulfuric acid and the appropriate alcohol. The relationship thus suggested was further proved: (1) by preparing azophenine from dianilinoquinone by the action of aniline and aniline hydrochloride; (2) by decomposition of azophenine into dianilinoquinone by means of concentrated sulfuric acid; and (3) by preparation of azophenine from dianilinoquinone anil by heating a long time with aniline at 180–200°.

The true empirical formula for azophenine—C₃₀H₂₄N₄—was confirmed by synthesis of various halogen-substituted derivatives. A few of the reactions studied are given herewith:

(1) The preparation of trichloroazophenine from *p*-chloroaniline, *p*-chloroaniline hydrochloride and *p*-nitrosodiphenylamine:

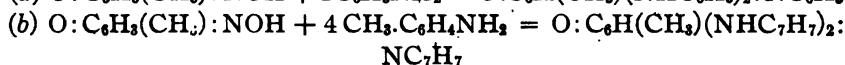
¹ Zincke and von Hagen, *Ber.* 16, 1553 (1883); *ibid.* 18, 788 (1885).



(2) The preparation of tetrachloroazophenine from *p*-chloroaniline and nitrosophenol:



(3) The formation of dianilinotoluquinone anil, and of ditoluinotoluquinone tolil, by the action of aniline and toluidine, respectively, with nitroso-*o*-cresol:



These three examples show that condensation evidently takes place between the amino group of the aromatic amine and the oxime group of the quinone oxime, or nitrosophenol. Just how the reaction goes forward is not so apparent. Reaction (3) further proves that a dianilinoquinone anil can be prepared from aniline and a nitrosophenolic compound. This fact agrees with the statement by Beilstein,¹ given under both nitrosophenol and azophenine, that aniline acetate and nitrosophenol yield phenylazophenol, azophenine and dianilinoquinone anil.

It is somewhat remarkable that in all of the foregoing work the formation of phenylazophenol receives so little attention.

III

THE REACTION OF *N*-CHLOROQUINONIMINE WITH AROMATIC AMINES

N-Chloroquinonimine (commonly called "quinonechlorimide") was first prepared by Schmitt and Bennewitz² who considered it to be orthodichloroazophenol. Its true constitution was determined by Hirsch,³ who prepared the compound by the action of sodium hypochlorite with *p*-aminophenol. He proved it to have the configuration:



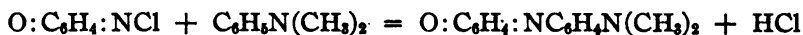
N-Chloroquinonimine has had considerable application in dye manufacture being said to react readily with amines and phenols forming indamines and indophenols. One method of preparing the so-called "Phenol

¹ Beilstein, II, 677; III, 341.

² Schmitt and Bennewitz, *J. prakt. Chem.* (116) N. F. 8, 1-10 (1874).

³ Hirsch, *Ber.* 13, 1903 (1880).

Blue" is by condensing dimethylaniline with *N*-chloroquinonimine:¹



It is also stated that *N*-chloroquinonimine mixed with amines or phenols forms indamines, or compounds which are the basis of certain "sulfur dyes."²

Strangely enough there is little reference in the literature to reactions involving *N*-chloroquinonimine and the simple, primary, aromatic amines. Schmitt and Andresen³ have investigated the action of *N*-chloroquinonimine and of trichloro-*N*-chloroquinonimine with aniline. When *N*-chloroquinonimine and aniline react "a violent, explosive-like reaction takes place * * * with much carbonization. In dilute alcohol the reaction runs more quietly but out of the brown mass, which remains after diluting the alcohol and removing the aniline with steam, a product pure enough for analysis could not be obtained." Schmitt and Andresen were able to purify the reaction product of trichloro-*N*-chloroquinonimine and aniline, however, obtaining anilinodichloroquinone.

With the same reagent and dimethylaniline they obtained a dyestuff:

$$\text{O}:\text{C}_6\text{HCl}_3:\text{NCl} + \text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2 = \text{O}:\text{C}_6\text{HCl}_3:\text{NC}_6\text{H}_4\text{N}(\text{CH}_3)_2 + \text{HCl}$$

IV

DISCUSSION OF EXPERIMENTAL RESULTS, AND CONCLUSIONS

1. *The mechanism of the nitrosophenol-aniline condensation.*

The first phase of the experimental work naturally had to do with the reaction between aniline and nitrosophenol. It was correlated by similar experiments with *p*-toluidine. Three principal reaction products were isolated, when condensations were carried on in the presence of glacial acetic acid, consisting of (1) phenylazophenol or hydroxyazobenzene, (2) dianilinoquinone anil, and (3) azophenine or dianilinoquinone dianil. All of these products have previously been mentioned as derived by this reaction but scant attention has been devoted to their significance insofar as the reaction mechanism is concerned.

By varying slightly such conditions as time, reaction temperature, etc., each of these compounds was obtained in fair yield and rather pure

¹ J. Fogh, *Ber.* 21, 887 (1888).

² French patent 378,665.

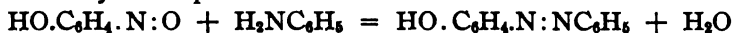
³ Schmitt and Andresen, *J. prakt. Chem.* 24, 426-43.

form. Furthermore, by very careful regulation of the acidity of the reaction mixture—sulfuric acid being used—a product was obtained which is undoubtedly an indophenol.

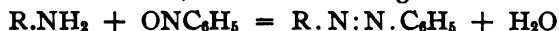
All condensations went forward only in acid solution. Attempts to carry on reactions under neutral or alkaline conditions invariably failed.

A consideration of the configuration of nitrosophenol and the probable mechanism of the reaction seems to provide but three ways in which it could take place:

(1) If nitrosophenol reacts as a true phenolic compound it may be represented by the equation:



Such a reaction might seem to be supported by the results of Kimich,¹ who obtained phenylazophenol when he carried out this reaction, and by our own confirmation of Kimich's results. Furthermore, the analogous reactions of primary aromatic amines with nitrosobenzene, with formation of azo derivatives, seems even stronger evidence:



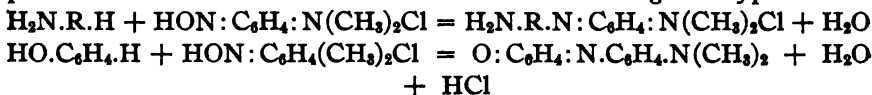
On the other hand it is difficult to understand why nitrosophenol, which functions normally as an oxime, should act as a true phenolic derivative in this particular case, especially since the tendency toward oxime formation, or configuration, is most striking in acid solutions. Furthermore, it is not at once clear why the amount of phenylazophenol obtained should be so small, or how the formation of the other known reaction products may proceed from this point.

The two other probable reactions are based upon an oxime configuration of nitrosophenol and may be represented as follows:



Thus by reaction (2) an indophenol (indoaniline) would be formed, or by reaction (3) quinone phenylhydrazone.

Evidence in favor of reaction (2), or indophenol formation, may be presented by means of a number of analogous reactions wherein such products are formed² and of which the two following are typical:



¹ Kimich, *loc. cit.*

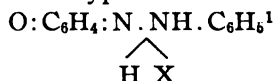
² Witt, *D. R. P.* 19224 (1882); Mohlau, *Ber.* 16, 2851 (1883).

That such indophenols or indamines may be formed in the course of the aniline-nitrosophenol reaction seems borne out by certain of our own experimental results; and it is reported that the reaction is used by some dye manufacturers in preparing this type of compound. However, it does not follow that indophenols are primary reaction products in this condensation, for here also, as in the case of the reaction (1) on page 13, it is difficult to understand how the remaining derivatives could be formed from indoaniline.

Reaction (3), however, may be made the basis of a scheme of reaction which, in our opinion, furnishes a satisfactory explanation for all reaction products and is supported by experimental proof.

It was found in carrying on the condensations that while some phenylazophenol was always formed the amount decreased as the time of reaction was increased. The total quantity in any case, more over, was relatively small. The bulk of the reaction products consisted of anilinoquinone derivatives. It was a question of whether the phenylazophenol was formed as the primary reaction product, and the anilino derivatives formed from it, or whether phenylazophenol was obtained by a secondary reaction from quinone phenylhydrazone. If the first idea is correct it should be possible to prepare anilinoquinones from phenylazophenol and aniline. Continued heating of aniline, or aniline hydrochloride, with free phenylazophenol produced no evidence of reaction. Quinone phenylhydrazone hydrochloride, which we have observed has the quinoid configuration, readily reacted with aniline forming dianilinoquinone anil.

It seems logical, therefore, to assume that the reaction begins with the formation of a quinone phenylhydrazone—as shown in reaction (3) on page 13. The stability of this compound is due to the simultaneous formation of an acid salt of the type



or of a hydrate which is relatively stable under the conditions of acidity obtaining. Such a hydrazone salt would explain the presence of phenylazophenol, its tautomer, as one of the reaction products. Furthermore, it seems clear that if the reaction be stopped after a short time the effect of adding an alkali would be the formation of a larger amount of phenylazophenol than if the reaction was permitted to run a long time. In the

¹ Hantzsch, *loc. cit.*

latter case an increased amount of the anilino derivatives should result with consequent decrease of the amount of free hydrazone present.

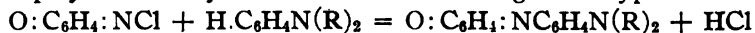
It is probable that the formation of quinone phenylhydrazone is accompanied almost simultaneously by formation of its anilino derivatives. The experiments of Hofman¹ and of Zincke and von Hagen² clearly show the great activity of the quinone nucleus in forming this type of compound; and the reaction of aniline with quinone phenylhydrazone hydrochloride is a case in point. That such derivatives are formed is further borne out by certain reaction products obtained when *N*-chloroquinonimine and aniline react; and which will be described below.

The evidence seems to indicate very clearly that the reaction proceeds by the formation of quinone phenylhydrazone and that mono- and dianilinoquinone phenylhydrazone derivatives are almost immediately formed therefrom. At the same time there results a small amount of phenylazophenol by tautomeric transition from the hydrazone and this decreases if the reaction proceeds a long time. The action of aniline upon the anilinoquinone phenylhydrazone derivatives results in the formation of dianilinoquinone anil and this latter compound reacts with still another molecule of aniline yielding azophenine, or dianilinoquinone dianil.³

2. *Theory of indophenol and indamine formation.*

The above scheme of reaction, however, does not account for the formation of indamines, or indophenols, which certain of the experimental results seem to demand. It is desirable, therefore, to extend it somewhat that this type of compound may be included in its scope.

The indophenols formed from primary amines are obtained only by very careful regulation of reaction conditions, as temperature, acidity, etc. Usually they are prepared by oxidation reactions between phenols and amines. Very few indophenol syntheses are recorded in which nitrosophenol is a reacting substance. With *N*-chloroquinonimine the instances are more numerous. The usual reaction described as a rule employs a tertiary amine and follows the general type:



But instances wherein primary amines so react are not often found.

¹ Hofmann, *Jahresbericht* 1863, p. 415.

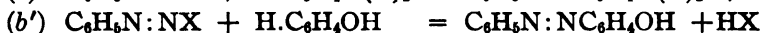
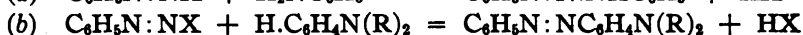
² Zincke and von Hagen, *Ber.* 16, 1555, 1558 (1883).

³ Fischer and Hepp, *loc. cit.*

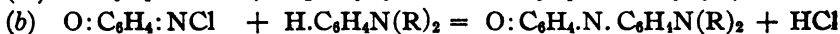
However, it is undoubtedly true that these very reactions may be employed in preparing indophenols when, by careful experiment, the exact conditions for effecting the synthesis have been determined.

By carrying on nitrosophenol-aniline condensations in very dilute sulfuric acid a black, amorphous reaction product was obtained which, by reduction with sodium sulfide and subsequent oxidation, gave a "sulfur blue" dye. That this black product was an indophenol there is no doubt.

Now, while the formation of indophenols takes place when tertiary amines are employed with nitrosophenol, it does not necessarily follow that identical reactions will take place when a primary amine is used and the amino group unsubstituted. On the contrary the evidence is in the other direction. For instance, when phenyldiazonium salts react with primary amines, and again with tertiary amines, or phenols, the products are entirely dissimilar:

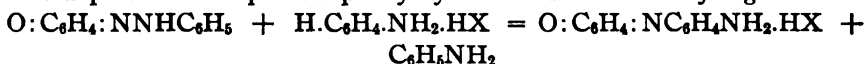


It is logical, therefore, to assume that the same is true with the nitrosophenol reaction, or *N*-chloroquinonimine:



In one of the reactions above, it may be noted that the preparation of azoaminobenzene was illustrated. It will be recalled that this compound undergoes a very curious and interesting rearrangement when treated with aniline hydrochloride, aminoazobenzene being formed: $\text{C}_6\text{H}_5\text{N}:\text{N.NHC}_6\text{H}_5 + \text{H.C}_6\text{H}_4\text{NH}_2.\text{HCl} = \text{C}_6\text{H}_5\text{N}:\text{NC}_6\text{H}_4\text{NH}_2.\text{HCl} + \text{C}_6\text{H}_5\text{NH}_2$

The use of a similar, or analogous, reaction to account for the formation of indophenol from quinone phenylhydrazone seems entirely logical:



3. The reaction of *N*-chloroquinonimine with aromatic amines.

With the object of correlating the foregoing reaction theory a number of experiments were tried using *N*-chloroquinonimine and primary aromatic amines—aniline and *p*-toluidine. The quinonimine has the same quinoid configuration as nitrosophenol:

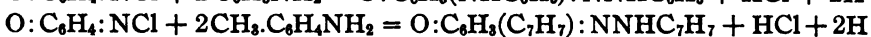


Such a compound might be expected to react in a similar way to nitrosophenol, assuming the latter functions as an oxime. Two reactions are possible in this case:



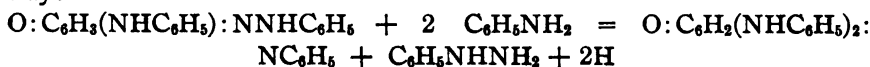
The first equation, wherein an indophenol is formed, coincides with a statement commonly found in textbooks of organic chemistry and dyestuffs. Actual references in the literature relative to such reactions, however, are rather limited and confined in a large measure to patent reports. A few references have already been made to reactions of this type. Most of them have dealt with the tertiary amines. Such work as has been carried on with the simpler aromatic primary amines has never led to definite results.

By carrying on a coupling reaction between *N*-chloroquinonimine and aniline we have obtained a reaction product, hitherto undescribed, which, from its method of formation, analysis, and reactions, appears to be the phenylhydrazone of monoanilinoquinone. This would confirm the accuracy of reaction (b) above. A similar *p*-toluinoquinone *p*-tolylhydrazone has been prepared using *p*-toluidine.



No dianilino- or ditoluinoquinone hydrazones were obtained.

When these products are digested in aniline they easily react forming the anil, and with the entrance of a second aniline residue into the nucleus. For instance, from anilinoquinone phenylhydrazone was obtained dianilinoquinone anil. The reaction probably takes place in the following way:

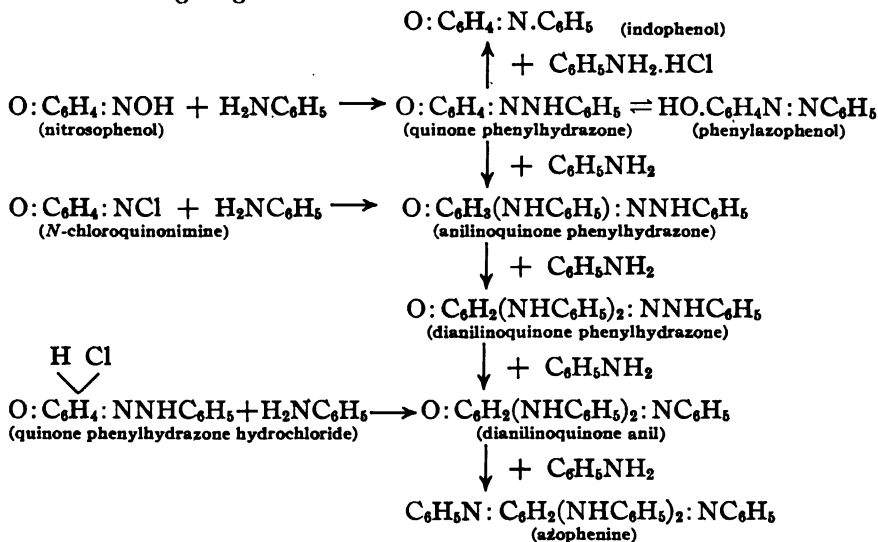


The significance of this reaction with regard to the mechanism of the nitrosophenol-aniline condensation is very clear. It supplies experimental proof that a direct transition may be accomplished from a quinone hydrazone to the corresponding anil; and shows that one of the intermediate products postulated in that reaction, but not isolated, really exists.

The assumption that the dianilinoquinone anil is really formed from a quinone hydrazone is given weight by the previously mentioned reaction of quinone phenylhydrazone, or phenylazophenol, hydrochloride and

aniline. This salt undoubtedly has a hydrazone configuration and di-anilinoquinone anil is quite easily obtained from it. The product of the *N*-chloroquinonimine-aniline reaction, reacting similarly, must have the hydrazone constitution.

The whole scheme of reaction and the relationships existing between the different compounds involved may be very clearly shown by means of the following diagram:



EXPERIMENTAL PART

PREPARATION OF NITROSOPHENOL

Nitrosophenol was prepared from phenol and nitrous acid by a modification of the method of Baeyer and Caro¹. Two hundred and seventy grams of pure phenol were melted and dissolved in 3713 cc. of distilled water. Two hundred and thirty grams of sodium nitrite, crushed in a mortar, were added in small portions with stirring throughout an hour. The solution was cooled to +6° C. and three hundred grams of concentrated hydrochloric acid (sp. gr. 1.19), diluted with 600 cc. of distilled water, were added to the reaction mixture at the rate of about thirty drops per minute, the stirring being continued. The mixture first became

¹ Baeyer and Caro, *Ber.* 7, 963. (1874).

black and tarry and later assumed a reddish tinge. After about the fifth hour of the addition of acid small crystals could be seen in the solution. After all the acid was added the stirring was continued for six hours at the same temperature. Six hundred grams of common salt were then added and the mixture stirred two hours longer, the temperature being maintained at 6 to 10°. The solid product was filtered onto a Buchner funnel and dried on a porous plate in air.

The crude product is dark red and decomposes slowly on standing in air but quite suddenly when heated between 110° and 125° C.

PREPARATION OF NITROSOPHENOL-SODIUM SALT

Crude nitrosophenol was purified by preparing the sodium salt and acidifying a solution of this substance when the pure product was desired.

To obtain the sodium salt the crude product, described above, was extracted several times with ether and the combined extracts concentrated by distilling off most of the solvent. To the reddish-brown solution obtained in this way a 40% solution of sodium hydroxide was added with stirring. A greenish-black slush resulted which was filtered by suction through an asbestos mat and dried. When dry the material is reddish-brown in color. Recrystallized from alcohol the salt is a beautiful dark red color and contains two molecules of water of crystallization. It is easily soluble in water and quite soluble in alcohol and benzene. In some of the following experiments a saturated alcoholic solution of the salt was used.

PREPARATION OF *N*-CHLOROQUINONIMINE

N-Chloroquinonimine (commonly called quinonechlorimide) is most conveniently prepared by the action of bleaching powder with *p*-aminophenol.

A very dilute solution of *p*-aminophenol was prepared and cooled to 0° C. A filtered solution of bleaching powder, similarly cooled, was added until a persistent yellow turbidity was obtained. The mixture was allowed to settle for some time and then filtered through a Buchner funnel. The *N*-chloroquinonimine is fairly pure in this form but was recrystallized from glacial acetic acid. Bright yellow plates melting at 84–85° C.

N-chloroquinonimine has a quinone-like odor and stains the skin. It is slightly soluble in water; more soluble in alcohol and ether. It darkens

in the light and must be kept in colored-glass bottles and out of the light so far as possible.

PREPARATION OF PHENYLAZOPHENOL HYDROCHLORIDE

This salt was prepared by taking up phenylazophenol (hydroxyazobenzene) in concentrated hydrochloric acid. The pasty red mass so formed was dissolved in glacial acetic acid and treated with an equal volume of concentrated hydrochloric acid. On standing the salt crystallizes in long, steel-blue needles, very similar in appearance to the crystals of the hydrochloride of aminoazobenzene (phenylazoaniline). They decompose slowly in air forming a maroon colored product which has the same properties as the original crystals. When treated with water the salt hydrolyzes giving phenylazophenol. The latter may also be formed by treatment of the salt with dilute caustic soda and reprecipitation with dilute acetic acid.

CONDENSATION OF NITROSOPHENOL WITH ANILINE

Condensations were carried on using both the free nitrosophenol and its sodium salt. The results were practically the same. When the free phenol was used it was freshly prepared by acidifying an aqueous solution of the sodium salt with dilute sulfuric acid and washing the precipitated material on the filter with ice water. In most of the condensations an alcoholic solution of the sodium salt was used. Such a solution contains 2.13 grams of salt per cubic centimeter.

By variation of the solvent and the time of reaction, varying amounts of the reaction products have been obtained.

I. *Condensation in alcoholic solution and in presence of acetic acid.*

The reaction products of aniline and nitrosophenol when condensed in alcohol and acetic acid are three in number: phenylazophenol, dianilinoquinone anil and azophenine. The presence of these three products in the reaction is proved by obtaining all of them in the pure condition. This portion of the work is, in part, a repetition of Kimich's experiments, and for the purpose of determining whether there is any evidence of a sequence of formation of the three products.

(1) *Preparation of Dianilinoquinone anil.*

Forty grams of sodium nitrosophenol in 200 cc. 95% alcohol (saturated solution) were treated with 40 grams of freshly distilled aniline dissolved in 115 cc. of glacial acetic acid. The mixture was heated slowly to the boiling point in a round bottom flask under a reflux condenser for thirty

minutes. It was then poured into a beaker, cooled, and let stand in the ice box for several hours. The solid separating was filtered off and washed three times on the filter with 95% alcohol. Dark purple needles. Yield 14 grams. The product was quite impure, doubtless containing some azophenine, and after three crystallizations from toluene melted at 182.4–183° C. By digesting in aniline for some time a product was obtained which, after recrystallization from xylene, melted at 193.5°.

By recrystallizing from xylene the compound is obtained as a brownish-red-purple mat of fine, hair-like crystals, insoluble in water, alkalis, alcohol and cold toluene and xylene, but readily soluble in chloroform. It dissolves in concentrated sulfuric acid forming a reddish-purple solution which heated to 300° passes through deep blue to greenish-blue. This solution upon dilution assumes a deep purple color.

Comparison with Dianilinoquinone anil.

A two gram sample of the above compound was digested a short time with aniline and recrystallized from xylene. It melted at 187°. This was mixed with a sample of dianilinoquinone anil having a melting point of 200.7°, and the two recrystallized together from xylene. The resulting mixture melts at 193°.

Comparison was made between the color reactions of the two compounds with sulfuric acid. They were found to be identical, going through deep blue to greenish-blue when heated above 300°. Both solutions give the same purple color on dilution.

Samples of dianilinoquinone anil and the above compound were analyzed for nitrogen:

Calculated for $C_{24}H_{19}N_3O \cdot H_2O$	N = 10.9%
Sample of dianilinoquinone anil	N = 10.5%
Sample of reaction product	N = 10.4%

In appearance the two compounds are exactly the same. The same is true of their solubilities. All the evidence, with the exception of slight discrepancies of melting point, seems to support the conclusion that the two compounds are identical. These differences, together with consideration of the difficulties which Kimich experienced in his analyses of the same reaction product, must be due to the fact that dianilinoquinone anil separates with water of crystallization which it does not lose below 150° C. The pure hydrate melts rather sharply at 187–188° while the anhydrous substance melts at 201° C. Mixtures melt intermediately.

(2). *Preparation of phenylazophenol, dianilinoquinone anil and azophenine.*

Twenty grams of pure sodium nitrosophenol were dissolved in 250 cc. of 95% alcohol and heated for thirty minutes at the boiling point with twenty grams of aniline in 60 cc. of glacial acetic acid. The reaction mixture was filtered immediately and left a residue of copper-bronze colored azophenine upon the filter. Upon recrystallization from toluene this product melted at 224.7° C.

A comparison of this product with pure azophenine was made in order to establish their identity. Pure azophenine melts at 236-7° but can be best detected by its characteristic color reaction with sulfuric acid. A concentrated sulfuric acid solution heated to 300° forms a dye known as fluorindine becoming light greenish-blue with a deep crimson fluorescence. Dilution leaves a sky-blue solution with the crimson fluorescence persisting. The compound prepared in the above reaction gave a corresponding series of color reactions. Its physical appearance and solubilities agree with those described for azophenine.

The filtrate was allowed to stand for several hours and the precipitate formed was removed and washed three times on the filter with 95% alcohol. The mother liquor yielded a second crop of crystals on further standing. Total yield 4 grams. This product was recrystallized from toluene and xylene and found to be identical with the crude dianilinoquinone anil described in experiment (1).

The mother liquor was poured into a large quantity of water (about two liters) and 250 cc. of dilute ammonia added. This mixture was heated to boiling and the tarry residue filtered off. The reddish-yellow solution was refiltered on cooling. It was then acidified with dilute acetic acid until a permanent turbidity was attained. Upon standing a yellow precipitate separated, which was filtered and washed with water. Yield 0.9 gram. This substance melted at 152-3°, and after recrystallization from a benzene-petroleum ether mixture, at 153.5°C. It is soluble in hydrochloric and sulfuric acids, and in sodium hydroxide solution with a red color; quite soluble in alcohol, ether and benzene. From the alkaline solution it may be reprecipitated by the addition of dilute acetic acid. In brief, it has all the properties peculiar to phenylazophenol, excepting that the melting point is slightly higher than that of the latter, according to descriptions in the literature.

Comparison with phenylazophenol

A small quantity of the reaction product was mixed with a sample of phenylazophenol melting at 149° and the mixture recrystallized from benzene-ligroin mixture. The recrystallized mixture melts at 151° C.

Analysis of the reaction product for nitrogen gave the following results:

Calculated for phenylazophenol. $C_{12}H_{10}N_2O$,	N = 14.14%
Found	N = 13.9%

The properties, melting point of the mixture, and analysis point to the conclusion that the reaction product is phenylazophenol.

(3) *Preparation of azophenine and phenylazophenol.*

Presence of dianilinoquinone anil was eliminated by increasing the time of reaction.

Twenty grams of pure sodium nitrosophenol were dissolved in 260 cc. of 95% alcohol, mixed with 20 grams of aniline in 60 cc. of glacial acetic acid, and heated to boiling under a reflux condenser for one hour. The reaction mixture was allowed to stand until completely cool and was then filtered by suction. Yield 1.3 grams of reddish-bronze plates, which after recrystallization from toluene melted at 225° . The compound gave the same series of color reactions when heated with concentrated sulfuric acid and is identical with azophenine.

The filtrate, which yielded no further precipitate on standing, was poured in a large amount of water and boiled with dilute ammonia. Upon filtering off the tarry material and treating the cooled solution with dilute acetic acid a precipitate of phenylazophenol was deposited. Yield 0.3 gram. The crude product melted at 153° C. and by recrystallization from a benzene-ligroin mixture its melting point was not raised. Its deportment with sulfuric acid and with dilute caustic soda solution is the same as that of a known sample of phenylazophenol, with which it is identical

(4) *Preparation of phenylazophenol and dianilinoquinone anil.*

Ten grams of pure sodium nitrosophenol were dissolved in 100 cc. of 95% alcohol and 10 grams of freshly distilled aniline, in 30 cc. of glacial acetic acid. The mixture was brought to boiling and held at that point for ten minutes, a reflux being used. It was then permitted to come to room temperature. A small sample diluted with water became turbid, the yellow color apparently denoting the presence of phenylazophenol.

After standing over night the solid material was filtered off and washed with alcohol. A small quantity of dark purplish crystals were obtained which were found to consist of crude dianilinoquinone anil.

The filtrate was diluted about five times and boiled with dilute ammonia. It was then cooled and the tarry material filtered off. The filtrate, treated with dilute acetic acid to incipient turbidity, yielded 0.5 gram of phenylazophenol.

Relation between quantities of phenylazophenol formed and time of digestion.

An interesting relationship may be noted in the above experiments between the time of reaction and the relative amounts of phenylazophenol formed:

Experiment (2). Twenty grams of nitrosophenol sodium salt gave 0.9 gram of phenylazophenol in 30 minutes.

Experiment (3). Twenty grams of nitrosophenol sodium salt gave 0.3 gram of phenylazophenol in 60 minutes.

Experiment (4). Ten grams of nitrosophenol sodium salt gave 0.5 gram of phenylazophenol in 10 minutes.

While these yields are not large, and were not measured with great accuracy, they nevertheless indicate that the amount of phenylazophenol obtained varies inversely with the time of reaction. In Experiment (4) the amount of phenylazophenol would probably be appreciably increased by extraction immediately after heating.

II. *Condensation in alcohol solution and in absence of acids.*

(5) *Attempt to condense free nitrosophenol and aniline.*

Thirty-five grams of freshly prepared nitrosophenol were dissolved in 350 cc. of 95% alcohol and 35 grams of freshly distilled aniline added. No action at room temperature could be observed. The mixture was heated under a reflux condenser for thirty minutes. A violent bumping was noticeable. The reaction mixture, which was brownish-green, was poured into a beaker and let stand over night at room temperature. A very small amount of tarry material separated which could not be purified.

When sufficient acetic acid was added to the filtrate to combine with the aniline present (25 grams of acetic acid were used) and the mixture heated under a reflux for thirty minutes a yield of azophenine was obtained. A portion of the filtrate from this reaction, treated with dilute ammonia and dilute acetic acid as in the preceding experiments, gave a small quantity of phenylazophenol, melting at 152.2–153°.

III. *Condensations in benzene solution and in presence of acetic acid.*

(6) *Formation of azophenine.*

The best yield of azophenine obtained through the nitrosophenol-aniline reaction was secured by use of benzene as a solvent. The time of reaction, however, was three hours and this may have been a factor.

Twenty-eight grams of sodium nitrosophenol were dissolved in 200 cc. of pure benzene by warming and twenty grams of aniline in 100 grams of glacial acetic acid added. The mixture was boiled three hours under a reflux condenser, going through a color change of brown to deep purple and finally to black at the end of the reaction. The mixture was allowed to cool to room temperature over night and then filtered, the product being washed in alcohol. A quantity of bronze-colored crystals were left upon the filter mixed with some darker impurity. When these were crystallized from a mixture of alcohol-benzene they melted at 233° C. The compound, when heated with sulfuric acid to 300°, gives the "fluor-indine" color reaction, which is characteristic of azophenine. The compound was further purified by digesting with aniline. Melting point 233-34° C.

The filtrate was concentrated upon the water bath and a black residue obtained which was easily recrystallized from toluene. This substance melts at 188° with decomposition. While it was not examined further it doubtless was an impure sample of dianilinoquinone anil.

IV. *Condensation in dilute sulfuric acid.*

(7) *Indophenol formation and preparation of "sulfur blue."*

The formation of certain sulfur dyes is based upon the reaction of nitrosophenol and aniline, or toluidine, in dilute sulfuric acid. The primary reaction product is considered to be an indophenol. This product is then reduced with sodium sulfide and oxidized to the dye by use of various oxidizing agents.

Several attempts were made to effect a condensation in dilute sulfuric acid solution in order to determine the character of the primary reaction. Although no direct evidence was obtained we are inclined to the opinion that the reaction goes in the normal way, *i. e.*, through the formation of a quinone hydrazone and thence to the indophenol.

Ten grams of sodium nitrosophenol were dissolved in 500 cc. of water containing 2.7 grams of sulfuric acid. To this was added a solution

of 5.3 grams of aniline in 500 cc. of water containing 5 grams of sulfuric acid. This mixture was stirred at room temperature for several days. Crystals of unchanged nitrosophenol were present in the solution for a long time but finally disappeared. A brownish foam was constantly present. Upon filtering a few grams of black material were obtained and purified by heating with water to 80°, the soluble impurities being filtered off. The undissolved residue was a clean, black, amorphous powder which sinters slightly at 207° but is not melted at 250°.

The filtrate was treated with a concentrated solution of sodium sulfide and the reaction made acid with dilute sulfuric acid. The solution upon heating became colorless. Some sulfur precipitated and was filtered off. The solution was then heated until hydrogen sulfide was completely driven out and then cooled in an ice bath. A white reduction product separated which turned blue on the filter before it could be dried, due to oxidation by air. The substance was dried in a vacuum dessicator. It is a dark blue color and from its mode of formation we believe it identical with the "sulfur blue" dye described as derived from aniline. The substance sinters at 140° and melts at 170–78° with decomposition. No attempt was made to purify it further as the quantity was small.

CONDENSATION OF *p*-TOLUIDINE WITH NITROSOPHENOL

I. *Condensations in alcohol and acetic acid.*

(8) *Formation of ditoluiñoquinone tolil.*

Forty grams of the sodium salt of nitrosophenol were dissolved in 200 cc. of 95% alcohol (saturated solution) and forty grams of *p*-toluidine, dissolved in alcohol, added, together with 115 cc. of glacial acetic acid. This reaction mixture was heated under a reflux condenser for thirty minutes, poured into a beaker and cooled in the ice box over night. The solid separating was filtered and washed three times with 95% alcohol on the filter. It is dark purple in color when recrystallized from toluene. Yield 9–10 grams. The substance gives a bluish-purple color with concentrated sulfuric acid which fades on heating to 300°.

(9) *Preparation of toluazophenine and tolylazophenol.*

Twenty grams of pure sodium nitrosophenol were dissolved in 200 cc. of 95% alcohol and mixed with a solution of twenty grams of *p*-toluidine in 60 cc. of glacial acetic acid. The reaction mixture was heated at the boiling point for thirty minutes under a reflux condenser and filtered

immediately. The residue is a reddish-brown color and was recrystallized from xylene. Melting point 232.5° . Yield 5.3 grams. The product is soluble in concentrated sulfuric acid with a bluish-purple color and corresponds to the description of toliazophenine, or ditoluinoquinone ditolil.

Analysis: Calculated for $C_{24}H_{32}N_4 \cdot H_2O$	N = 10.89 %
Found	N = 10.77 %

The filtrate was poured into a large amount of water and heated to boiling with dilute ammonia. A mass of tarry material was formed which was filtered off. The filtrate was reddish-yellow and was treated with dilute acetic acid until a permanent turbidity was obtained. On standing a yellow deposit of *p*-tolylazophenol separated which was filtered and dried. Melting point of crude product 147.2° . Yield 0.4 gram. This was dissolved in dilute sodium hydroxide, forming a reddish-yellow solution, and reprecipitated with dilute acetic acid. It then melted at 148° . A known sample of *p*-tolylazophenol melted at 151° . The substance gives a red compound with concentrated sulfuric acid and this is hydrolyzed to yellow tolylazophenol by treatment with water. Its identity with tolylazophenol seems unquestioned.

REACTIONS OF *N*-CHLOROQUINONIMINE WITH THE PRIMARY AROMATIC AMINES

(10) *Preparation of anilinoquinone phenylhydrazone.*

Ten grams of *N*-chloroquinonimine were dissolved in 350 cc. of 95% alcohol and ten grams of redistilled aniline added with stirring. The temperature of the reaction mixture was 15 to 20° C. In a few moments shiny particles could be seen floating about in the solution and after standing several hours the whole mass solidified. It was placed upon a filter, sucked dry, and washed with a small amount of hydrochloric acid diluted with alcohol. When dry it is a dark brown powder with purplish cast. Yield 13 grams.

To purify this substance was a very painstaking task. It was first treated with dilute ammonia containing a small quantity of alcohol (to insure thorough wetting) and heated to boiling. The undissolved material was filtered off and thoroughly washed with cold water. When dry this product is light brown. Yield 10 grams. It was recrystallized in small portions from a mixture of alcohol-benzene (1:3), about 100 cc. of solvent being needed for every gram of solid material. Each portion was heated

to boiling on an electric hot plate and filtered hot. On standing a solid separates as a brick-red amorphous powder. Yield 2 to 3 grams. This powder was recrystallized from toluene, or xylene, the same proportion of solvent being needed as with the alcohol-benzene mixture. Yield of the purified product 2 grams.

Anilinoquinone phenylhydrazone forms beautiful, shiny, maroon-colored crystal plates which decompose between 228 and 235° C. It is insoluble in alcohol and ether, and only slightly soluble in hot toluene or xylene; insoluble in water and alkalis. In acids it is soluble after long standing. A red solution is formed with concentrated hydrochloric acid; a light reddish solution with nitric acid which fades. With sulfuric acid a reddish-purple solution is produced which changes on heating through clear, deep blue to a light indigo-blue color. Upon dilution this color fades to a very faint purple and can be reduced to a colorless condition by zinc and acetic acid.

Analysis: Calculated for $C_{18}H_{16}N_2O.H_2O$	N = 13.61 %
Found	N = 13.63 %

(II) *Preparation of dianilinoquinone anil by action of aniline with anilinoquinone phenylhydrazone.*

Aniline reacts readily with anilinoquinone phenylhydrazone forming dianilinoquinone anil. Digestion of the hydrazone was carried on in hot aniline for a few minutes and the reaction mixture cooled. It was filtered and the precipitate washed with alcohol and dried. After several recrystallizations from xylene the product melted at 197.3°. A sample of dianilinoquinone anil melting at 200.7° was mixed with the reaction product and the two compounds crystallized together. This mixture melted at 199–201.5°.

In appearance and many other physical properties the anil is very similar to anilinoquinone phenylhydrazone. They crystallize in the same habit and have like solubilities. The color reaction with concentrated sulfuric follows an identical course, going through reddish-purple, deep blue and finally indigo-blue at 300°. On diluting this hot solution however, the anil gives a clear, deep purple color, whereas the hydrazone gives only a *faint* purple coloration.

Analysis: Calculated for $C_{24}H_{18}N_2O.H_2O$	N = 10.96 %
Found	N = 10.56 %

Molecular weight:	Calculated	383
	Found	383
	Found	397

(12) *Action of aniline with N-chloroquinonimine in glacial acetic acid.*

Five grams of *N*-chloroquinonimine were dissolved in 75 grams of glacial acetic acid and mixed with a solution of 10 grams of aniline in 25 grams of glacial acetic acid. The two solutions were mixed with stirring, the temperature being maintained at 10°. The yellow color of the quinone was discharged at once and after stirring for two hours the mixture was left stand over night. A light brown product was obtained on filtering which was heated with water to 80° and filtered from the soluble impurities. However, the material obtained was so impure as to show a very indefinite melting point. Decomposition began at 171° but the compound was not melted up to 200° C. Attempts to crystallize it from the ordinary organic solvents met with no success. Upon digesting with hot aniline dianilinoquinone anil is quickly formed.

(13) *Preparation of p-toluiquinone p-tolylhydrazone.*

Thirteen grams of *N*-chloroquinonimine were dissolved in 500 cc. of 95% alcohol by warming and added to a solution of thirteen grams of *p*-toluidine in 100 cc. of alcohol. The reaction began at once and after several hours standing the solid material was removed by filtration, washed with an alcoholic solution of hydrochloric acid, and dried. Yield 13 grams of dark purplish-red powder.

The product was purified by treating with 250 cc. of dilute ammonia and a little alcohol, and heating to boiling. After filtering and drying the undissolved material there remained 12 grams of a brown powder. This was first recrystallized from a mixture of alcohol-benzene (1:3) by dividing it into one gram portions and heating each portion carefully to boiling with about 100 cc. of the solvent mixture; the solutions were filtered hot and the filtrates left stand in the ice box several hours. Four grams of red powder were obtained which was finally recrystallized from toluene, in which it is only slightly soluble. Yield of purified product, 3 grams.

After several recrystallizations from toluene a product was obtained melting at 217.3–221° with decomposition. The compound forms in small, hair-like crystals of a bright purplish-red color. It is insoluble

in water, alcohol and ether, and only slightly soluble in hot toluene and xylene. Insoluble in alkalies and slightly soluble in acids. With concentrated sulfuric acid it gives a beautiful blue coloration which gradually fades if heated to 300° C.

Analysis: Calculated for $C_{20}H_{19}N_3O \cdot H_2O$	N = 12.53 %
Found.	N = 12.18 %

One attempt to effect a reaction with aniline was unsuccessful, no solid reaction product being obtained.

REACTION OF ANILINE WITH PHENYLAZOPHENOL HYDROCHLORIDE

(14) *Preparation of dianilinoquinone anil.*

One gram of phenylazophenol hydrochloride was dissolved in ten grams of freshly distilled aniline by heating to the boiling point for a few moments on an electric hot plate. On cooling, and after standing for a short time, a crystal mass was formed which was filtered by suction and thoroughly washed with alcohol. After two recrystallizations from toluene this product melts at 198–200° C.

Comparison was made with dianilinoquinone anil by mixing with the above product a sample having a melting point of 200–203°. The mixture was recrystallized and melts at 200–203° C. The color reaction with sulfuric acid, previously described, was employed here and found to give results identical with those obtained in the case of dianilinoquinone anil.

(15) *Attempt to condense aniline with phenylazophenol.*

One gram of free phenylazophenol was heated with ten grams of aniline at the boiling point for ten minutes. No solid reaction product separated even after the mixture had stood for several hours. A similar experiment with aniline acetate gave the same results. By taking up the material in acetic acid and adding dilute caustic soda solution unchanged phenylazophenol is precipitated.

SUMMARY

It is shown that the three condensation products of aniline with nitroso-phenol form a sequence: phenylazophenol, dianilinoquinone anil and azophenine.

By the reaction of aniline with *N*-chloroquinonimine an analogous sequence of reaction products is developed. In this case the presence

of phenylazophenol is not proved but a new product, monoanilinoquinone phenylhydrazone, is described and shown to fit into the scheme between the phenylazophenol stage and dianilinoquinone anil.

Quinone phenylhydrazone is assumed to be the first condensation product. The presence of phenylazophenol during the early stages of the reaction is accounted for by its tautomerism with quinone phenylhydrazone.

It is proven that quinone phenylhydrazone hydrochloride is easily transformed into dianilinoquinone anil by the action of aniline.

The full sequence of condensation products formed by the action of aniline upon either nitrosophenol or *N*-chloroquinonimine is quinone phenylhydrazone, monoanilinoquinone phenylhydrazone, dianilinoquinone anil and azophenine.

To explain the formation of the simple indophenols quinone phenylhydrazone is assumed as the first condensation product. This substance yields the indophenol by a rearrangement perfectly analogous to that by which *p*-aminoazobenzene is formed from diazoaminobenzene.

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AUTOBIOGRAPHY

I, Carleton Edgar Curran, was born at New Lexington, Ohio, September 23, 1890. My elementary and secondary education was received in the public school and high school of that village, and my undergraduate college training at the Ohio State University and Wabash College. I received the Bachelor of Arts degree from the latter institution in 1912. In 1915 I was granted the degree of Master of Arts by the Ohio State University. From 1916 to 1918 I was connected with the editorial staff of *Chemical Abstracts* and then enlisted in the Chemical Warfare Service of the United States Army serving until the end of the war. In February 1919 I was appointed Du Pont Research Fellow at The Ohio State University and completed the requirements for the degree of Doctor of Philosophy at the end of the summer session in 1920, the degree being conferred in June, 1921.

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